

HINDERED DIFFUSION OF COAL AND PETROLEUM ASPHALTENES IN A SUPPORTED HYDROTREATING CATALYST

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ABSTRACT

In this work, hindered diffusion of one coal and two petroleum asphaltenes was studied by adsorptive uptake in THF from a bath surrounding a commercial $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst. A mathematical model for the adsorption-diffusion of asphaltenes was developed. The model parameters were obtained by simulating the experimental data with the model solution. Several asphaltene fractions were defined via SEC (size exclusion chromatography), with the molecular weight of each fraction being determined by its elution characteristics using polystyrene standards. It was found that both the coal and petroleum asphaltenes have very broad molecular weight distributions; however, the molecular weights of the coal asphaltenes (50-1000) were much smaller than those of the two petroleum asphaltenes (300-10000 and 300-20000 respectively). The uptake rates for asphaltene fractions with different molecular weights were different, depending on their diffusion rates and adsorption capacities. Simulation results showed that even though the properties of coal and petroleum asphaltenes were quite different, the values of model parameters for the fractions of the three asphaltenes had the same trend; with increasing molecular weight of the fraction, the adsorption constant monotonically increases, and the effective diffusivity decreases. The experimental diffusion data of the three asphaltenes were well represented by similar mathematical models.

INTRODUCTION

Due to comparable sizes of reactant molecules and catalyst pores, hindered diffusion has been widely observed in the hydrotreatment of asphaltenes, heavy oils, coal derived liquids, and other macromolecular feeds. Direct measurements of asphaltene intrapore diffusion in porous catalysts are recent and very few in number. Baltus and Anderson (1983) studied hindered diffusion of petroleum asphaltenes through membranes, in which several fractions were defined by SEC according to their elution characteristics. Mieville et al. (1989) measured the diffusion of petroleum asphaltenes through porous materials by uptake experiments, in which the asphaltenes were treated as monodispersed and a linear adsorption isotherm was obtained.

In this work, hindered diffusion of coal and petroleum asphaltenes in THF was studied by adsorptive uptake experiments from a bath surrounding a commercial $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst. The asphaltenes were grouped into several fractions via SEC. An adsorption-diffusion model was developed for the uptake process. The objective of this work was to see if the diffusion uptake could be represented by a single mathematical model using reasonable parameter values.

EXPERIMENTAL

Materials. One coal and two petroleum asphaltenes, denoted as C-97500, P-AAK and P-AAG, respectively, were used in the diffusion study. The coal and petroleum asphaltenes, defined as THF(tetrahydrofuran) solubles and n-pentane insolubles, were extracted from a coal resid and petroleum asphalts, respectively. HPLC grade THF was used as solvent in the uptake experiments. Toluene and polystyrenes with narrow molecular weight distributions were used as calibration standards for analysis of asphaltenes on SEC. A commercial unimodal catalyst, Criterion 324, with an average pore diameter of 125 Å, was used in this study. Catalyst samples were crushed to -12+16 mesh size (-1.0+1.4 mm in diameter) and calcined at 673 K for 12 hours prior to use in uptake experiments.

Apparatus and Procedures. Diffusion experiments were performed in a magnetically stirred glass diffusion cell containing a screen wire basket for holding catalyst particles at 308 K. Catalysts were presaturated with THF before diffusion runs, during which the uptake of asphaltenes was monitored periodically by analyzing the concentration of asphaltenes in the bath solution using SEC.

SEC with a UV detector at 262 nm wavelength was used to analyze the concentration of asphaltenes in THF. Four μ -styragel columns, with nominal pore sizes of 1000, 1000, 500 and 500 Å respectively, were used in series for the SEC. A computer data acquisition system was employed to record the UV absorbance vs. elution time of the effluents. HPLC grade THF was used as mobile phase at 1 cm³/min.

HINDERED DIFFUSION MODEL FOR ASPHALTENES

A mathematical model was utilized to describe the behavior of hindered diffusion of asphaltenes in porous catalyst particles. The asphaltenes are grouped into different fractions according to their molecular weights ascertained from SEC analysis. The porous catalyst particles were immersed in a well-stirred bath containing asphaltenes and solvent. The asphaltene molecules diffuse into the porous particle where they are adsorbed onto the solid catalyst surface. As a result of this diffusion-adsorption process, the concentration of asphaltenes in the surrounding bath is depleted. However, due to the difference in adsorption capacity and diffusion rate of each asphaltene fraction, the depletion rates for different asphaltene fractions will be different.

The hindered diffusion model developed here assumes negligible solute transport by surface diffusion, spherical catalyst particle geometry, uniform pore size distribution along the particle radius, negligible external fluid solid mass transfer resistance, and local adsorption equilibrium inside the particle pores (Yang and Guin, 1996a, 1996b). It is also assumed that the adsorption isotherm is linear for each fraction, and the properties of each fraction, e.g., molecular size, diffusivity, and adsorption capacity, are independent of every other fraction during the adsorption-diffusion process. With the above assumptions, the adsorption-diffusion mathematical model can be developed and solved analytically (Bird et al., 1960), with the dimensionless bath concentration of asphaltene fraction j being expressed as a function of dimensionless time by,

$$\theta_{bj} = \frac{B_j}{1+B_j} + 6B_j \sum_{k=1}^{\infty} \frac{\exp(-b_k^2 t_j^*)}{B_j^2 b_k^2 + 9(1+B_j)} \quad (1)$$

where, the b_k 's are the non-zero roots of

$$\tan(b_k) = \frac{3b_k}{3+B_j b_k^2} \quad (2)$$

and

$$\theta_{bj} = \frac{C_{bj}}{C_{bjo}}, \quad B_j = \frac{V_b}{V_p} \frac{1}{K_{pj}\epsilon + \rho_p K_j}, \quad t_j^* = \frac{D_{ej}}{R^2} \frac{1}{K_{pj}\epsilon + \rho_p K_j} t \quad (3)$$

In the above equations, D_{ej} is the effective diffusivity expressed as,

$$D_{ej} = \frac{K_p K_{\eta} \epsilon}{\tau} D_{mj} \quad (4)$$

in which K_p and K_{η} factors are hindered diffusion parameters due to steric and hydrodynamic effects, respectively, being estimated by,

$$K_{pj} = (1-\lambda_j)^2 \quad (5)$$

$$K_{\eta} = 1 - 2.104\lambda_j + 2.089\lambda_j^3 - 0.948\lambda_j^5 \quad (6)$$

For a hydrodynamic diffusion solute, the molecular diffusivity D_{mj} is related to the solute size by the Stokes-Einstein equation,

$$D_{mj} = \frac{kT}{6\pi\eta_0 r_{mj}} \quad (7)$$

For a typical adsorptive diffusion system, the values for most parameters in the model are known except those for K_j (or B_j) and D_{ej} . The values of these two parameters can be obtained by fitting the mathematical model to the experimental asphaltene uptake data.

RESULTS AND DISCUSSION

1. Asphaltene Molecular Weights

SEC analysis of asphaltenes requires the use of calibration standards to determine the average molecular weights of the fractions from elution volumes. Several investigators have used polystyrenes as calibration standards to obtain the equivalent molecular weight distributions of heavy oils and asphaltenes (Song et al., 1991; Baltus and Anderson, 1983; Sanchez et al., 1984; Dark and McGough, 1978). By comparing the molecular weights of prefractionated heavy oil fractions obtained from VPO

(vapor pressure osmometry) and polystyrene calibrated SEC, some studies showed that both measurements agreed well at least in some range (Brule, 1981; Bartle et al., 1984; Baltisberger et al., 1984;). However, others stated that there were differences between these two methods (Kiet et al., 1977; Wong and Gladstone, 1983). It might appear that the VPO method would give more accurate molecular weights; however, Nali and Manclossi (1995) stated that VPO molecular weight measurement failed when strong interactions among single molecules, e.g., highly aromatic compounds, were present. Mieville et al. (1989) showed that different asphaltenes with the same VPO molecular weights could elute at different volumes on SEC, inferring the absence of a universal relationship between SEC and VPO molecular weights for different asphaltenes. In the absence of any clear correlation between VPO and SEC molecular weights, we have used polystyrenes as SEC standards to calibrate the molecular weight distribution of our coal and petroleum asphaltenes.

Toluene and polystyrene standards with weight average molecular weights ranging from 92 to 14000 were first dissolved in THF. These solutions were analyzed via SEC, and the logarithm of molecular weights of the standards vs. elution volumes is shown in Figure 1, resulting a good linear fit being expressed as,

$$\log(M_w) = -0.125V_R + 7.261 \quad (8)$$

Figure 2 shows SEC chromatograms of the coal and petroleum asphaltenes in THF. There are two x-axes in this figure, one is the elution volume, the other is the equivalent polystyrene/toluene molecular weight calculated from equation (8). It is observed that the equivalent molecular weights of the coal asphaltenes, 50-1000, are much smaller than those of the petroleum asphaltenes (300-20000 for P-AAK and 300-10000 for P-AAG). In the simulation of experimental asphaltene diffusion data, several fractions of the asphaltenes will be defined in terms of the equivalent eluted polystyrene/toluene molecular weights.

2. Effective Diffusivities and Adsorption Constants of Asphaltene Fractions

As seen in the model development section, to perform the model simulation for uptake of each asphaltene fraction, the effective diffusivity D_e and the adsorption parameter K_d are required. One method for determination of the molecular diffusivities of asphaltene fractions is to assume that they are the same as those of the polystyrene standards with same elution volumes. However, Baltus and Anderson (1983) showed that these two values are different, with the molecular diffusivities of polystyrenes being roughly two times of those of petroleum asphaltene fractions. Viewed in another way, if we know the size r_m of each asphaltene fraction, the molecular diffusivity can be calculated from equation (7). Nortz et al. (1990) measured hydrodynamic properties of prefractionated heavy oils in THF and obtained the following relationship between the molecular radius in Å and VPO molecular weight,

$$r_m = 0.36 M_w^{0.50} \quad (9)$$

In equation (9) the molecule radius was calculated from the Stokes-Einstein equation using the molecular diffusivity experimentally determined by Taylor dispersion measurements. We have assumed that the above equation is applicable to our coal and petroleum asphaltenes, and that the molecular weights from VPO can be represented by those from SEC. With these assumptions, the molecular diffusivity of any asphaltene fraction eluted in SEC can be estimated through equation (7). The results for some asphaltene fractions are shown in Table 1. Comparison of the molecular weight ranges in Figure 2 with Table 1 shows that the effective diffusivities for the coal asphaltenes are in the range of $3\text{--}30 \times 10^{-7}$, while the ranges for the two petroleum asphaltenes P-AAK and P-AAG are $5\text{--}10000 \times 10^{-10}$ and $6\text{--}1000 \times 10^{-9} \text{ cm}^2/\text{s}$, respectively.

Due to the instability of asphaltenes in THF solvent, it is difficult to obtain the adsorption constants K_d from equilibrium experiments; however, this value can be ascertained by fitting the experimental diffusional uptake data with the model solution given by equation (1).

3. Simulation of Asphaltene Diffusion into Porous Catalyst

In our diffusion study, one coal and two petroleum asphaltenes were used as solutes. Figures 3, 4 and 5 (points) show the uptake data for the three asphaltenes in THF on Criterion 324 catalyst, respectively. It is seen from these figures that as diffusion time increases, the UV absorbances or concentrations of the coal asphaltenes fractions and most petroleum asphaltene fractions in the bath solution decrease. However, the rates of decrease for asphaltene fractions with different molecular weights are different, depending on their diffusion rates and adsorption capacities. It is interesting that for the two petroleum asphaltenes, as shown in Figures 4 and 5, respectively, some cross-overs of the SEC data were observed at higher molecular weights (approximately greater than 10000). In other words, the molecular weight distribution shifted to higher molecular weights during the uptake process, resulting in increasing bath concentrations for these fractions. A possible reason for this unusual phenomena might be the agglomeration of smaller molecules into larger ones. This aspect of the work needs further investigation.

For the numerical simulation of the experimental uptake results for the three asphaltenes, we first group the SEC data into several fractions, each with an elution volume of 0.5 cm³. Some of the estimated effective diffusivities for these fractions are shown in Table 1. For each fraction, the dimensionless bath concentration θ_{ij} can be obtained by the ratio of the area under SEC curve at time t to that at time $t=0$. The adsorption constant K_j can be obtained by fitting the experimental (θ_{ij} , t) data with the model solution for each fraction. Figure 6 shows the values of adsorption constant K_j for different asphaltene fractions. It is seen that even though the properties of the three asphaltenes are quite different, as shown in Figure 2, the values of adsorption parameters for the fractions of these asphaltenes have the same trend; with increasing the molecular weight, the adsorption constant monotonically increases. It has also been observed (Takahashi et al., 1980; Dimino, 1994) that adsorption of polymers in porous materials increased as the molecular weights increased. Best fits of adsorption constant vs. molecular weight for the fractions of the three asphaltenes can be obtained with power regression from the data points in Figure 6, being expressed as,

$$\begin{aligned} \text{C-97500: } K_j &= 3.352 M_{wj}^{0.530} \\ \text{P-AAK: } K_j &= 0.0239 M_{wj}^{1.246} \\ \text{P-AAG: } K_j &= 0.105 M_{wj}^{1.151} \end{aligned} \quad (10)$$

It should be pointed out that for the two petroleum asphaltenes P-AAK and P-AAG in the above equations, we used fractions of molecular weights less than 10000. Beyond this value some of the experimental bath concentrations increased as discussed above and could not be fitted by the uptake model. In the simulation of the experimental uptake data with the model solution, adsorption constants K_j for fractions of molecular weights larger than 10000 were instead obtained by extrapolation of the above equations.

As long as the relationship between the adsorption constant K_j and the molecular weight is determined, the diffusion equation (1) can be solved for any asphaltene fraction eluted from SEC. The simulated model solution for the three asphaltenes are also shown in Figures 3, 4 and 5 (lines), respectively. It is observed that for the coal asphaltenes, the model fits experimental data quite well, as seen from Figure 3. For the two petroleum asphaltenes, the model fits the experimental data fairly well in smaller molecular weight regions, as shown in Figures 4 and 5 respectively; however, in the larger molecular weight regions, some departures were observed due to the cross-overs of the experimental uptake data, particularly at longer diffusion times.

CONCLUSION

Both the coal and petroleum asphaltenes used in this study have very broad molecular weight distributions, with the molecular weights of the coal asphaltenes (50-1000) being much smaller than those of the petroleum asphaltenes (300-20000 for P-AAK and 300-10000 for P-AAG). The coal asphaltene fractions have estimated effective diffusivities which span 1 order of magnitude, whereas these spans are more than 2 orders for the fractions of the two petroleum asphaltenes. The uptake rates for asphaltene fractions with different molecular weights are different, depending on their diffusion rates and adsorption capacities. Even though the properties of the asphaltenes used are quite different, the values of model parameters for the fractions of the three asphaltenes have the same trend; with increasing molecular weight of the fraction, the adsorption constant increases and the effective diffusivity decreases monotonically. The experimental diffusion data for the three asphaltenes can be represented fairly well in most molecular weight regions by the same mathematical model using appropriate parameter values.

Acknowledgment

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Nomenclatures

B	dimensionless model constant
C_b	bath concentration
C_{b0}	initial bath concentration
D_m	molecular diffusivity, cm ² /s
D_e	effective diffusivity, cm ² /s
k	Boltzmann's constant, 1.38×10^{-6} erg/°K
K	linear adsorption constant, cm ³ -solution/g-catalyst
K_p	partition factor
K_r	restriction factor

M_w molecular weight, g/mol
 r_m molecule radius, Å
 R radius of catalyst particle, cm
 t time, h
 t^* dimensionless time
 T temperature, °K
 V_b bath volume, cm³
 V_p catalyst pore volume, cm³
 V_R elution volume on SEC
 ϵ catalyst porosity
 η_0 solvent viscosity, g/cm-s
 θ_b dimensionless concentration in bath
 λ ratio of solute molecule diameter to catalyst pore diameter
 ρ_p catalyst particle density, g/cm³
 τ catalyst tortuosity factor

Subscript

j j th asphaltene fraction defined on SEC

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Table 1. Estimated effective diffusivities and other parameters at 35 °C

elution vol., cm ³	M_w^a g/mol	r_m^b Å	D_m^c cm ² /s	D_e^d cm ² /s
23	24322.0	56.1	7.9E-07	1.3E-10
25	13677.3	42.1	1.1E-06	2.2E-09
27	7691.3	31.6	1.4E-06	1.3E-08
29	4325.1	23.7	1.9E-06	4.9E-08
31	2432.2	17.8	2.5E-06	1.3E-07
33	1367.7	13.3	3.3E-06	2.6E-07
35	769.1	10.0	4.5E-06	4.6E-07
37	432.5	7.5	5.9E-06	7.6E-07
39	243.2	5.6	7.9E-06	1.2E-06
41	136.8	4.2	1.1E-05	1.7E-06
43	76.9	3.2	1.4E-05	2.5E-06
45	43.3	2.4	1.9E-05	3.5E-06
47	24.3	1.8	2.5E-05	4.9E-06

a. Determined by equation (8).

b. Estimated from equation (9).

c. Calculated from equation (7) with THF viscosity of $4.42 \cdot 10^{-3}$ g/cm-s (Reid et al., 1987).

d. Determined by equation (4) with $\epsilon=0.66$ and $\tau=3.0$.

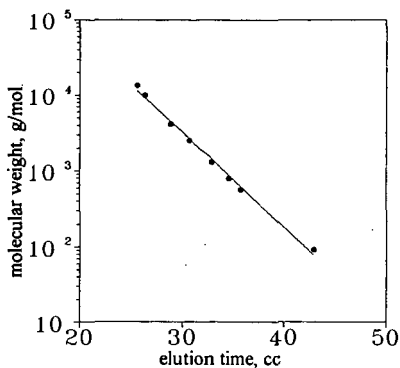


Figure 1. Calibration of SEC columns by toluene and polystyrenes.

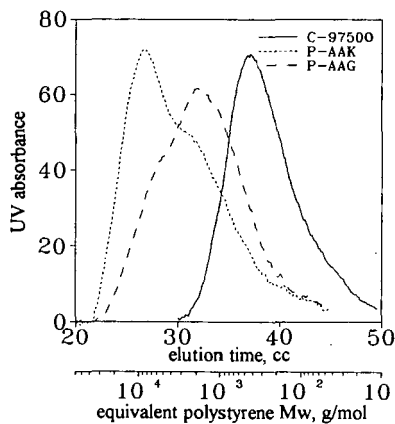


Figure 2. Comparison of SEC Mw distributions in THF for coal and petroleum asphaltenes.

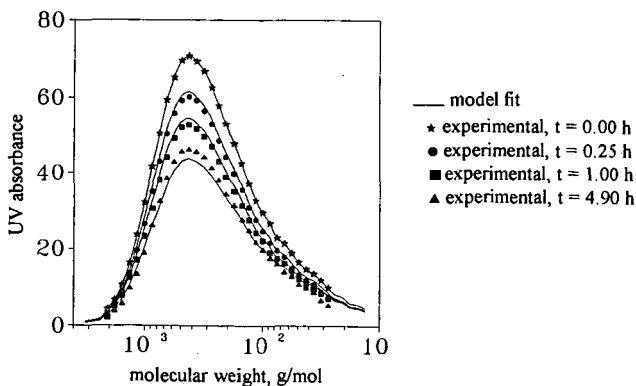


Figure 3. Simulation of experimental uptake data with math model for diffusion of coal asphaltenes in THF into Criterion 324 catalyst at 35 °C.

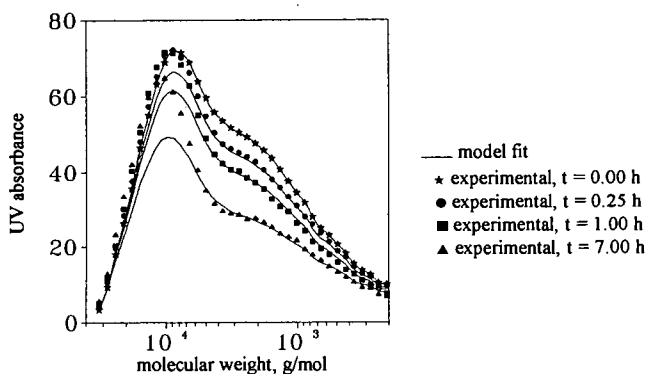


Figure 4. Simulation of experimental uptake data with math model for diffusion of P-AAK asphaltenes in THF into Criterion 324 catalyst at 35 °C.

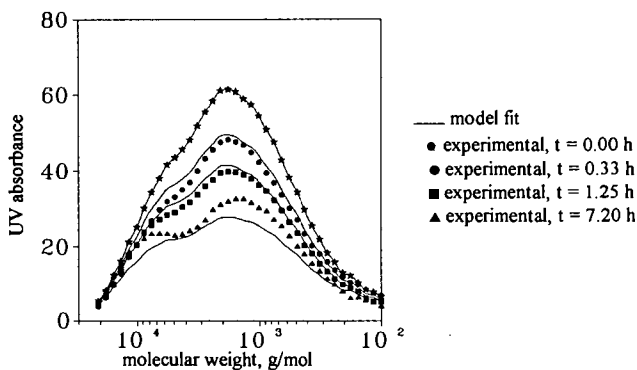


Figure 5. Simulation of experimental uptake data with math model for diffusion of P-AAG asphaltenes in THF into Criterion 324 catalyst at 35 °C.

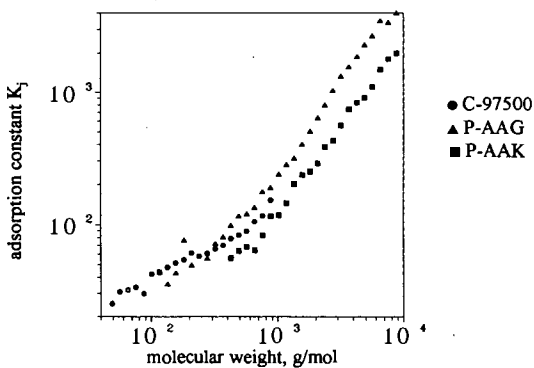


Figure 6. Relationship between molecular weight and adsorption constant for coal and petroleum asphaltenes.